Calhoun
Institutional Archive of the Naval Postgraduate School

Calhoun: The NPS Institutional Archive

DSpace Repository

Theses and Dissertations | 1. Thesis and Dissertation Collection, all items

1961

Measurement of transference numbers of the bisulfate ion in aqueous sulfuric acid.

Gardner, Howard W.

http://hdl.handle.net/10945/12635

Downloaded from NPS Archive: Calhoun

DUDLEY KNOX LIBRARY

http://www.nps.edu/library

Calhoun is the Naval Postgraduate School's public access digital repository for research materials and institutional publications created by the NPS community. Calhoun is named for Professor of Mathematics Guy K. Calhoun, NPS's first appointed -- and published -- scholarly author.

Dudley Knox Library / Naval Postgraduate School
411 Dyer Road / 1 University Circle
Monterey, California USA 93943

NPS ARCHIVE
1961
GARDNER, H.

MEASUREMENT OF TRANSFERENCE NUMBERS OF THE BISULFATE ION IN AQUEOUS SULFURIC ACID

HOWARD W. GARDNER

DUDLEY KNOX LIBRARY
NAVAL POSTGRADUATE SCHOOL
MONTEREY CA 93943-5101

LIBRARY
U.S. NAVAL POSTGRADUATE SCHOOL
MONTEREY CALIFORNIA

MEASUREMENT OF TRANSFERENCE NUMBERS OF THE BISULFATE ION IN AQUEOUS SULFURIC ACID

* * * * *

Howard W. Gardner

MEASUREMENT OF TRANSFERENCE NUMBERS OF THE BISULFATE ION IN AQUEOUS SULFURIC ACID

by

Howard W. Gardner
Lieutenant, United States Navy

Submitted in partial fulfillment of
the requirements for the degree of

MASTER OF SCIENCE

United States Naval Postgraduate School
Monterey, California

1961

NPS Archive
1961
Gardner, H.

Library
U. S. Naval Postgraduate School
Monterey, California

MEASUREMENT OF TRANSFERENCE NUMBERS OF THE BISULFATE ION IN AQUEOUS SULFURIC ACID

by

Howard W. Gardner

This work is accepted as fulfilling
the thesis requirements for the degree of
MASTER OF SCIENCE
from the
United States Naval Postgraduate School

ABSTRACT

The unusually high mobility of the hydrogen ion and the hydroxide ion in water has been ascribed to a proton transfer chain mechanism. In recent years it has been demonstrated that a similar mechanism results in abnormal mobility of the bisulfate ion in absolute sulfuric acid. In an effort to determine the nature of the mechanism in the transition from chain conductance by the hydronium ion to chain conductance by the bisulfate ion in aqueous sulfuric acid solutions, Hittorf transference numbers were measured for the bisulfate ion in aqueous sulfuric acid above 70% acid by weight.

The transference numbers measured ranged from 0.07 to 0.14. The transference numbers obtained in these measurements are the result of physical migration only and not a proton jump chain transfer; hence these values may be considered as a confirmation of the existence of a chain mechanism in this concentration range, but do not permit further determination of the nature of the chain mechanism. It is estimated that approximately two-thirds of the current is carried by a proton transfer chain conductance mechanism in the vicinity of the monohydrate composition.

The writer wishes to express his appreciation for the assistance and encouragement given by Professor Richard A. Reinhardt of the U. S. Naval Postgraduate School in this investigation.

TABLE OF CONTENTS

Section	Title	Page
1.	Introduction	1
2.	Experimental Procedure	4
3.	Experimental Results	15
4.	Conclusions	22
	Bibliography	23
Appendix I	Composition of Sulfuric Acid Solutions	25
Appendix II	A Model of the Conductance Mechanism in Sulfuric Acid	30

LIST OF ILLUSTRATIONS

Figure		Page
1.	Properties of Sulfuric Acid Solutions	3
2.	Transference cell	5
3.	Electrolysis circuit	8
4.	Bisulfate ion transference numbers	17
II-1	Conductivity according to model	39
II-2	Transference numbers according to model	44

1. Introduction

The abnormally high conductance of the hydrogen ion in water has been known for many years and has been explained by a type of Grotthus chain mechanism [1, 2, 7]. Hammett and Lowenheim [9] measured the transference numbers of barium and strontium ions in sulfuric acid and found that almost none of the current was being carried by the cation; they proposed a similar mechanism of chain conductance in sulfuric acid. More recent work, especially that of Gillespie and Wasif [4, 6, 17], has substantiated this theory. Similar abnormal mobility of the hydrogen ion has been found in other hydrogen-bonded solvents. In general, there are apparently two principal types of chain conductance mechanisms: conductance by an excess proton, and conductance by a defect proton. In the water system, the hydrogen ion conducts by the excess proton mechanism, and the hydroxide ion conducts by the defect proton mechanism. Similarly, in sulfuric acid the $H_3SO_4^+$ ion conducts by an excess proton mechanism, and the HSO_4^- ion conducts by a defect proton mechanism.

The autoprotolysis of water is given by:

(1) $$2\ H_2O = H_3O^+ + OH^-$$

In sulfuric acid the autoprotolysis is represented by:

(2) $$2\ H_2SO_4 = H_3SO_4^+ + HSO_4^-.$$

In solutions of water in sulfuric acid, the ionization of the water at low water concentration is essentially complete [3]:

(3) $$H_2O + H_2SO_4 = H_3O^+ + HSO_4^-$$

This ionization represses the autoprotolysis of the solvent; therefore, to

a good approximation, in solutions with the mole fraction of sulfuric acid greater than 0.5, the ionic species present will be the hydronium ion and the bisulfate ion.

At the concentration of the monohydrate of sulfuric acid, the numbers of H_2SO_4 molecules and H_2O molecules will be equal. There should, therefore, be approximately equal opportunity for proton defect conductance of the HSO_4^- ion through the sulfuric acid molecules and for the excess proton conductance of the H_3O^+ ion through the water molecules. Transference number measurements were made on the sulfuric acid itself in the concentration range from 30 to 85 mole percent H_2SO_4 in the hope that information could be obtained for comparison of the two conductance mechanisms.

The physical properties of aqueous sulfuric acid show remarkable variation in the vicinity of equal molar concentration (see Fig. 1). There is a maximum of viscosity almost exactly at the monohydrate composition [12]. Similarly there is a conductivity minimum at a mole fraction of sulfuric acid slightly above 0.50 [11]. The viscosity-conductivity product shows a sudden change between 40 and 50 mole percent sulfuric acid. These variations are undoubtedly related to molecular association phenomena. The hope that transference number measurements might provide additional insight into the variations of the conductivity in this region provided additional motivation for this study. Unfortunately, the results obtained do not permit much more than confirmation of the existence of the chain conductance mechanism in this concentration range.

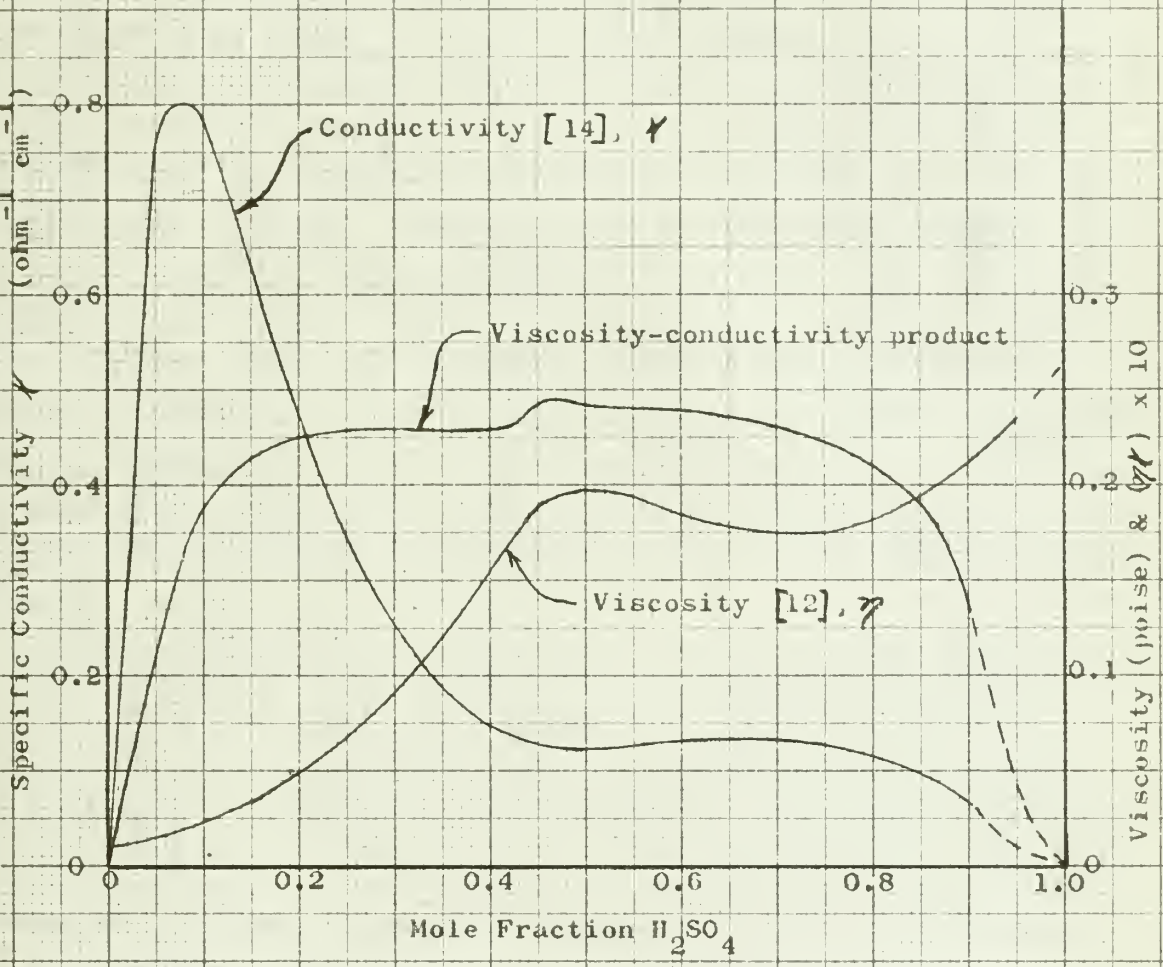

Figure 1

Properties of Sulfuric Acid Solutions

2. Experimental procedure.

Transference numbers of the bisulfate ion were measured by the Hittorf method in the system water-sulfuric acid in the concentration range above 70% sulfuric acid by weight. The Hittorf method was chosen for these measurements when consideration of other methods showed this to be the only satisfactory method for direct transference number measurements in this system. There is insufficient knowledge of the system in this range to permit selection of an appropriate indicator for use in the moving boundary technique. The cell potential method used by Hamer at lower concentrations requires a large number of consecutive cell potential measurements; the number of measurements required becomes excessive at higher concentrations because of heat of dilution effects [8]. Furthermore, for the purpose of this study, it is impossible to say with the cell potential measurements whether the conductance is by a chain mechanism or by migration.

Initially an attempt was made to use a transference cell similar to that of Hammett and Lowenheim [9], modified to permit separation of the cell compartments for weighing. Difficulties were encountered in maintaining the liquid junction, probably as the result of an air leak in the joint or stopcock. Furthermore the rather fragile legs of the liquid bridges were quite susceptible to breakage. Consequently, this design was finally abandoned and the design shown in Fig. 2 was adopted.

In this cell the three electrolyte compartments were standard eight-inch Pyrex test tubes. The liquid bridges were eight-millimeter Pyrex tubing, the atmospheric openings of which were closed by rubber tubing and pinchclamps. These liquid bridges could thus be filled by means of a vacuum, and they provided a ready means of separating the electrolyte at

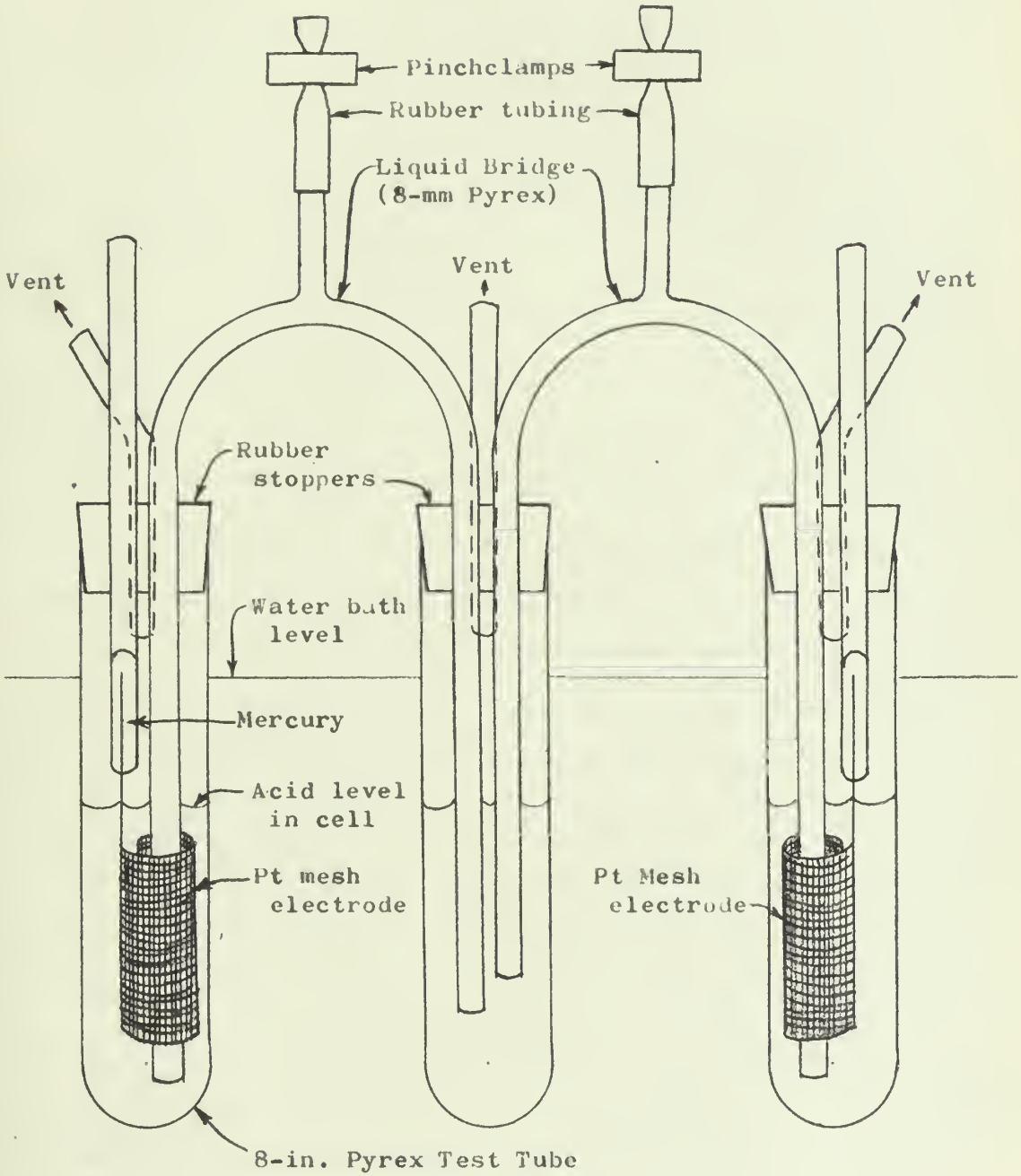

Figure 2

Transference Cell

the end of each run. Rubber stoppers were used as an expedient; however, attack by sulfuric acid was rapid enough to make glass preferable. Acid attack on the rubber stoppers was reduced by wrapping the stoppers with commercial saran film. The cell was mounted on a removable "Flexoframe" support in the water bath during electrolysis.

The electrodes were of bright platinum mesh and were sealed in six-millimeter soft glass tubing. Electrical connections to the external circuit were made by a liquid mercury junction. Considerable difficulty was encountered in the problem of electrode selection. Hammett and Lowenhein [9] reported the formation of ozone and other oxidizing agents at the anode and the formation of sulfur dioxide and free sulfur at the cathode. Experimentation confirmed the liberation of free sulfur and sulfur dioxide at the cathode. Experiments were conducted with Hg, Hg_2SO_4 electrodes, but they were unsuccessful; gas evolution and the liberation of free sulfur were reduced but not eliminated. The unknown products of the cathode reaction made data from the cathode compartment useless. It was possible in the analytical procedure to compensate for any peroxy sulfates formed at the anode. Production of ozone and hydrogen peroxide would not affect the results because of the requirement for electroneutrality. Therefore, it was possible to make all runs with bright platinum electrodes regardless of the electrode reactions which might occur. The cathode compartment was ignored, and only the anode and center compartments were analyzed.

Electrolysis was carried out using the circuit of Fig. 3. The recording millivoltmeter was calibrated for current measurement by direct comparison with the milliammeter. The average current could thus be determined from the record of the millivoltmeter. The recorder was used in place of the usual silver or copper coulometer since other errors in the procedure

would probably negate any increased accuracy gained by use of the more accurate coulometers.

In conducting the electrolysis, the anode compartment test tube was weighed dry to the nearest hundredth gram on a hanging-pan triple-beam balance. The three test tubes were filled to the desired level with stock acid of approximately the desired concentration. The electrode and liquid bridge assembly was then put in place, and the liquid junctions were filled. The entire assembly was then placed in the water bath, where the cells were immersed to the level indicated in Fig. 2. The temperature of the water bath was thermostatically controlled to 25°C. The solution was electrolyzed for 23-26 hours at about 30 ma. During electrolysis the acid was protected from moisture by silica gel drying tubes connected to the vents. Upon completion of the electrolysis, the liquid seals were broken, the anode compartment was removed and weighed, and samples were taken from the anode and center compartments and were titrated with sodium hydroxide.

The acid solutions were made by diluting 96% C.P. reagent grade sulfuric acid to the desired strength. Sodium hydroxide solutions were prepared from Baker and Adamson 50% sodium hydroxide solutions. The sodium hydroxide solutions were standardized against Baker and Adamson A. C. S. reagent grade potassium acid phthalate, minimum assay 99.9%.

Three samples of about five grams of acid each were taken from each compartment to be analyzed; the actual sample size was determined by the acid concentration to suit the analytical procedure. Samples were weighed to the nearest tenth milligram in covered sample bottles and then quantitatively transferred to a flask for titration. 100 ml. of approximately 0.8 M sodium hydroxide was added by pipette; then titration to the end point was completed with 0.2 M sodium hydroxide using phenolphthalein as an

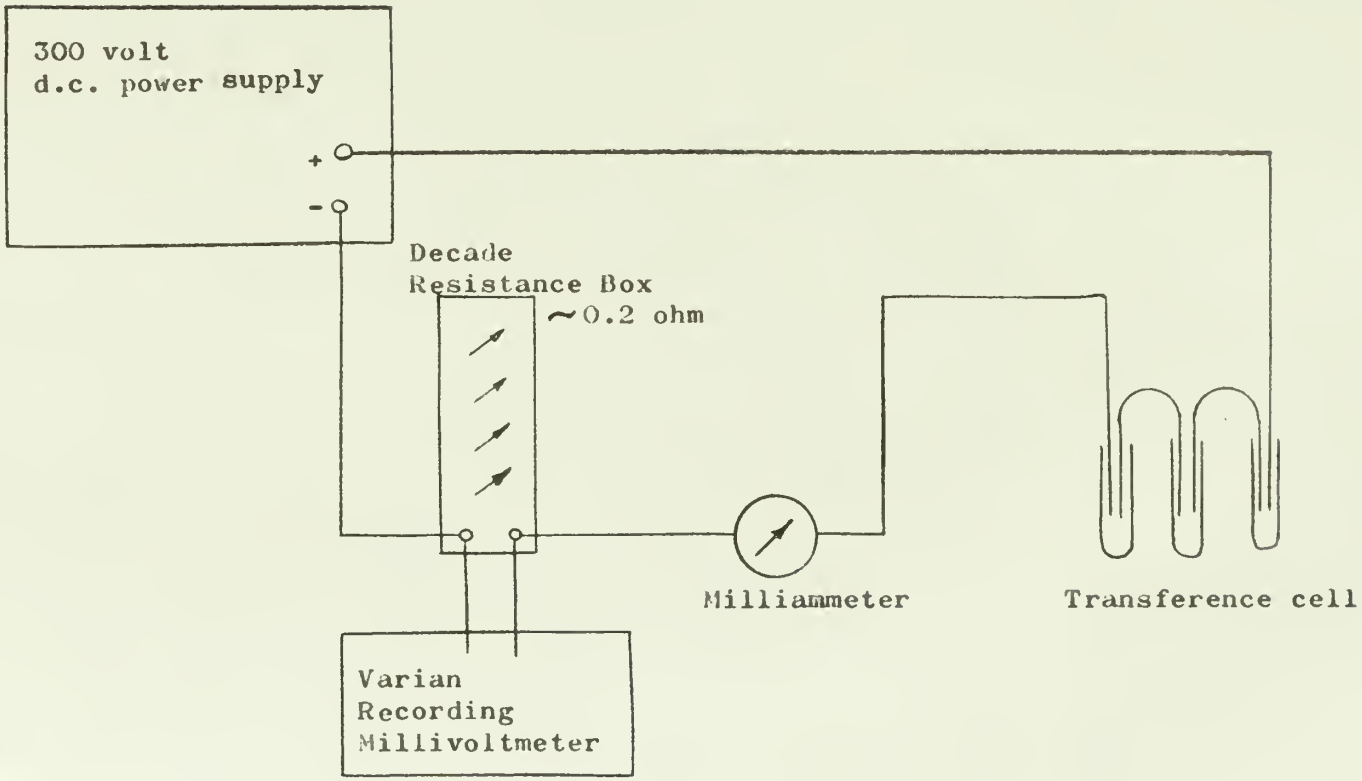

Figure 3

Electrolysis Circuit

indicator.

The 0.8 M sodium hydroxide was standardized against potassium acid phthalate by titration of 100 ml of the base from the pipettes used in the acid titrations with an approximately 0.38 M solution of potassium acid phthalate made by dissolving a weighed portion of the standard in water and diluting to one liter. The 0.2 M sodium hydroxide was standardized by titration of weighed portions of potassium acid phthalate with the base. The procedures reduced the error in volume measurement caused by wall retention of the solution.

The anode reaction may produce ozone, peroxymonosulfate, and peroxydisulfate as well as free oxygen. Ozone production would not interfere with the above analytical procedure since the hydrogen ion produced per faraday is the same as that produced in liberation of free oxygen. The peroxysulfates, however, would introduce an error due to the different acid equivalence per faraday for the production of peroxymonosulfuric acid and peroxydisulfuric acid. To compensate for this possibility, a modification of the procedure of Treadwell and Hall [16] which utilized hydrolysis of the peroxysulfates was used. After the endpoint was reached in the titration, the solution was boiled about 30 minutes. If a detectable amount of persulfate were present, the solution would now be acidic and additional titration to a second end point would permit treating the data as if no peroxysulfates had formed. The technique was tried with known acid and potassium persulfate mixtures and found to be quite satisfactory, the results checking to about one part in 10,000 for total acid after hydrolysis of the persulfate. It was noticed in these practice titrations that the presence of the persulfate rendered the first end point indefinite but that the second was sharp. In the actual runs there never was a detectable

change in the end point after boiling; this indicates that peroxysulfate formation was too slight to be significant.

Since subsequent reduction of data was based on the assumption that the anode reaction is entirely represented by:

(4) $3\ H_2O = \frac{1}{2}\ O_2 + 2\ H_3O^+ + 2\ e^-$

it is necessary that any side reactions either must not affect the analytical data or must be compensated for by the analytical procedure. That the above procedure satisfies these requirements is shown by consideration of the reactions involved. The probable side electrode reactions are:

(5) $2\ HSO_4^- = H_2S_2O_8 + 2\ e^-$

(6) $HSO_4^- + 2\ H_2O = H_2SO_5 + H_3O^+ + 2\ e^-$

(7) $9\ H_2O = O_3 + 6\ H_3O^+ + 6\ e^-$

(8) $4\ H_2O = H_2O_2 + 2\ H_3O^+ + 2\ e^-$

From equations (7) and (8) it can be seen that the production of ozone or hydrogen peroxide results in the formation of one mole of hydrogen ion per faraday, which is the same result as that obtained from reaction (4). These reactions therefore will not interfere with the analysis of data on the assumption of equation (4).

The peroxydisulfate hydrolyzes in steps as follows [13]:

(9) $H_2S_2O_8 + H_2O = H_2SO_4 + H_2SO_5$

(10) $H_2SO_5 + H_2O = H_2SO_4 + H_2O_2$

(11) $H_2O_2 = H_2O + \frac{1}{2}\ O_2$

The sum of these equations with the appropriate electrode reaction leads to an equation equivalent to equation (4). The hydrolysis of persulfate

according to these reactions is the basis for the quantitative analytical procedure given by Treadwell and Hall [16]. Since the hydrolysis proceeds through all the probable side reaction products except ozone, the hydrolysis, as adapted to this procedure should provide satisfactory compensation for the side reactions. The net effect of this hydrolysis is that the total base used will be the same as if all the acid had existed as H_2SO_4 and the electrolysis had proceeded entirely according to equation (4).

The reduction of data was accomplished essentially according to the method of Weissberger [18]. In each compartment of the transference cell

(12) $$(n_R)_{final} = (n_R)_{initial} + (\Delta n_R)_{el.rn.} + (\Delta n_R)_{migr.}$$

where: $(n_R)_{final}$ = number of moles of component R in the compartment after electrolysis.

$(n_R)_{initial}$ = number of moles of component R in the compartment before electrolysis.

$(\Delta n)_{R\ el.rn.}$ = change in the number of moles of component R in the compartment by electrode reaction.

$(\Delta n_R)_{migr.}$ = change in the number of moles of component R in the compartment by ion migration.

In the analytical scheme used for this work, the component detected is total acid, which is equivalent to solely H_2SO_4. Since the sulfuric acid does not enter into the effective electrode reaction, and because of the requirement for electroneutrality, $(\Delta n_{H_2SO_4})_{el.rn.}$ is equal to zero, and:

(13) $$(n_{H_2SO_4})_{final} - (n_{H_2SO_4})_{initial} = (\Delta n_{H_2SO_4})_{migr.}$$

The effects of chain conductance in the anode compartment are best represented by the reactions:

(14) $H_2SO_4 = HSO_4^- + p^+$

(15) $H_3O^+ = H_2O + p^+$

The protons represented in these equations are removed from the anode compartment by chain transfer; the net effect in the compartment is the formation of bisulfate ions and water molecules from sulfuric acid molecules and hydronium ions. In order to find the relation between actual physical migration of bisulfate ion and the analytical data, material balances were written for the anode compartment. For these material balances the following quantities were used:

a = the number of moles of HSO_4^- which entered the anode compartment by physical migration, per faraday of total charge transfer.

b = the number of moles of HSO_4^- formed in the anode compartment by chain conductance, in accordance with equation (14), per faraday of total charge transfer.

c = the number of moles of H_3O^+ which were transferred out of the anode compartment by physical migration, per faraday of total charge transfer.

d = the number of moles of H_3O^+ which were decomposed in the anode compartment according to equation (15), per faraday of total charge transfer, as a result of chain conductance.

Since the conductance is considered to result from the combination of these two mechanisms alone and these ions are estimated to be the only ions present in significant numbers, the following relation results:

(16) $1 = a + b + c + d$

The electrode reaction is assumed to be entirely represented by:

(4) $3\ H_2O = \frac{1}{2}\ O_2 + 2\ H_3O^+ + 2\ e^-$

The following changes in number of moles present in the anode compartment thus occurred per faraday:

	Change in Number of Moles			
	H_3O^+	HSO_4^-	H_2SO_4	H_2O
electrode reaction	+ 1			- 3/2
ion migration	- c	+ a		
chain transfer	- d	+ b	- b	+ d
total	1 - c -d	a + b	- b	-3/2 + d

Furthermore, electroneutrality requires:

$$1 - c - d = a + b$$

which is in accordance with equation (16). The equilibrium represented by:

(3) $H_3O^+ + HSO_4^- = H_2O + H_2SO_4$

must exist at all times. Since the analytical procedure determines the total sulfuric present in both the ionized and the unionized forms, the total change in moles of sulfuric acid in the anode compartment during electrolysis is:

(17) $$\Delta n_{H_2SO_4} = q\left[(a + b) - b\right] = qa$$

where: q = the total charge transfer in faradays

Since the electronic charge on the bisulfate ion is one, the number of equivalents transferred per faraday is equal to a; this is by definition the transference number of the bisulfate ion [18]. Therefore the transference number of the bisulfate ion is given by:

$$(18) \qquad T_{HSO_4^-} = a = \frac{\Delta n_{H_2SO_4}}{q}$$

According to the analytical procedure used:

$$(19) \qquad n_{H_2SO_4} = \frac{1}{2}\left[\left(\frac{\text{no. equivalents NaOH}}{\text{no. g. acid sample}}\right)_{\text{final}} - \left(\frac{\text{no. equiv. NaOH}}{\text{no. g. sample}}\right)_{\text{initial}}\right] \times \text{sample wt. (g)}$$

The analysis produced $\Delta n_{H_2SO_4}$ by application of equation (19) which, in combination with the charge transferred, permitted calculation of the bisulfate ion transference number according to equation (18). This transference number, as shown above, results only from the physical migration of the bisulfate ion and not from the effective migration resulting from conductance by the proton transfer chain mechanism.

3. Experimental results.

A total of fourteen experimental runs were made. The first one was not used because proper precautions had not been taken against moisture, and it was made with a Hg, Hg_2SO_4 cathode which did not function properly throughout the run. One was discarded because the samples taken were too small and the end point was over-run on addition of the 100 ml. of 0.8 M NaOH. One run was spoiled by the addition of the 0.8 M NaOH solution before the base had been standardized; the base was then found to be approximately half strength. Another run was spoiled by failure to record the final weight of the anode compartment. The results of the remaining ten experimental runs are shown in Table 1 and are plotted in Fig. 4.

The calculation of the transference numbers involves small differences between two numbers of nearly the same size. The major sources of error would thus be errors affecting the values of these two concentrations. The numbers were such that an error in analysis of one part in 15,000 would result in an error of about one percent in the transference number. In general, the precision of the analyses was such that the accuracy of the analyses was estimated as only about one part in 1,500. From this it is estimated that the error in the result from analytical errors may be as high as about 20%, assuming that the combination of errors from the two analyses is such that the probable error is equal to $\sqrt{2}$ times the error resulting from a single analytical error.

Absorption of atmospheric moisture would be an appreciable source of error if the analysis did not depend on the difference between the compositions of two solutions which had been exposed to essentially the same atmospheric conditions. Since the center compartment and the anode compartment were in a similar environment at all times and since the acid

Table 1
Experimental Results

Run	Charge Trans. (coul)	Wt. of Anode Soln (g)	Analyses (equiv/g. soln) Stock Acid	Anode Compt.	Center Compt.	△ equiv g. soln	$T_{HSO_4^-}$	Mole % H_2SO_4
2	1997	60.97		.018291	.018238	.000053	.090	60.9
3	1860	71.94	.017066	.017090	.017036	.000054	.101	48.3
4	3107	63.17	.017052	.017182	.017042	.000140	.137	48.3
5	2804	53.20	.017052	.017151	.017018	.000138	.126	48.3
6	2451	55.88		.017128	.017032	.000096	.106	48.3
8	3030	53.70	.019634	.019732	.019647	.000085	.071	83.0
9	2750	53.59		.019716	.019589	.000127	.120	81.8
11	2380	50.07	.014514	.014653	.014506	.000140	.143	31.2
12	2310	45.81	.014514	.014655	.014507	.000148	.143	31.2
14	2619	58.31	.017899	.018011	.017900	.000111	.119	57.1

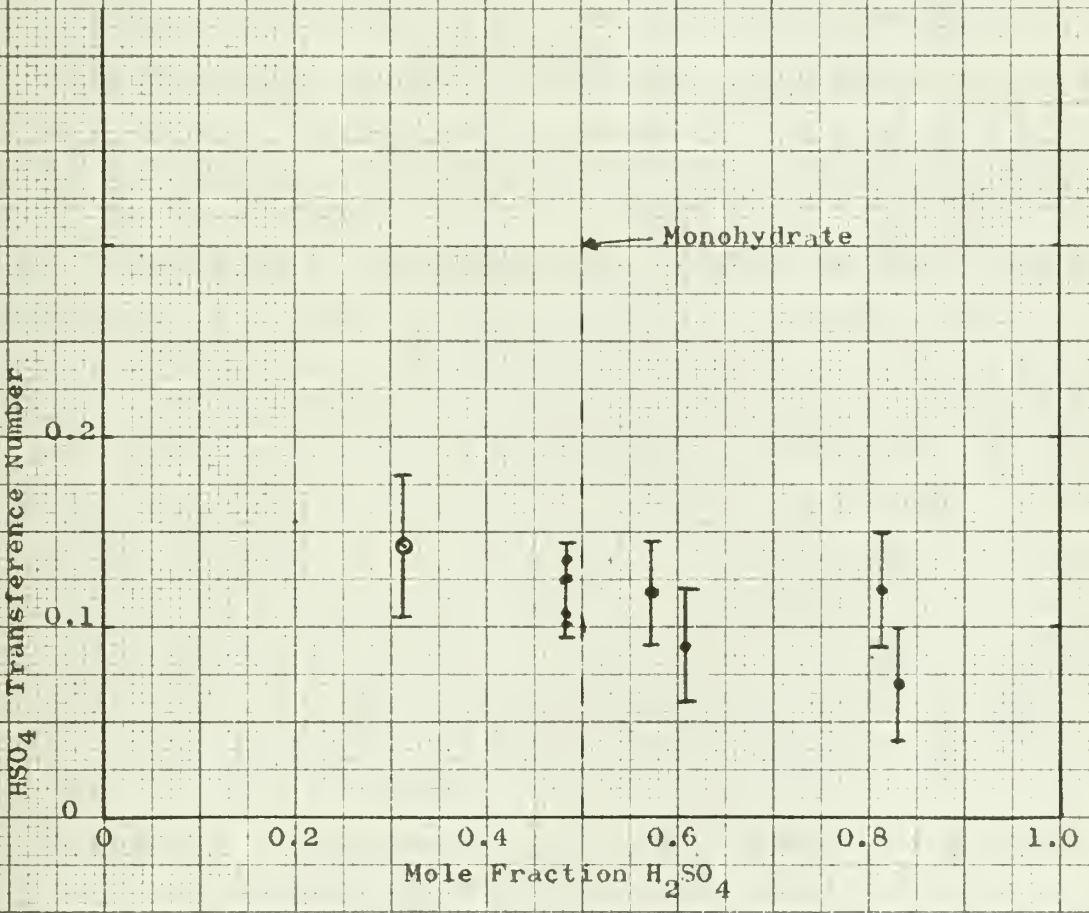

Figure 4

Bisulfate Ion Transference Numbers

compositions were approximately equal, it may be assumed that the absorption of atmospheric moisture was approximately the same in each compartment. The error from this source should then be small in comparison with the other errors.

A small mass change will occur as a result of gas evolution during electrolysis. For oxygen evolution this loss would amount to about 0.2 gram or about one part in 300. A small loss of acid, probably of the order of one half gram will occur by physical removal with the electrode assembly. This loss will introduce another error of the order of one percent.

Thermal diffusion errors may have existed but were probably negligible in comparison with the other errors. The design of the transference cell did not permit cooling of the liquid bridges in the thermostat. Free sulfur formed in the catholyte and its diffusion through the liquid bridge could be observed. In no case was the free sulfur observed to move over one third of the way up the leg of the bridge; this indicates that the effect of diffusion on the results should be small.

Errors from measurement of the average current arise from calibration of the millivoltmeter and variation of current. The calibration is only accurate in this case to about one-fourth milliampere; this represents an error of approximately one percent. The current varied in distinct steps with the operation of the thermostat on the water bath; the difference in current caused by this effect was approximately one milliampere. This variation showed up on the recorder trace as short pips. The current was averaged based on the high value then adjusted downward to correct for the lower average value. The errors from this effect are estimated to be negligible in comparison with the other errors.

In aggregate, it is estimated that the accuracy of the transference

numbers obtained is of the order of $\pm$ 25%. This estimated accuracy is indicated in Fig. 4.

As a first check on the results, Walden's rule [10] was applied. According to this rule:

(17) $\eta \lambda_j$ = constant

where: λ_j = ionic conductance of species j

η = viscosity of the solution

This relation was extended to estimate:

(18) $\eta_0 \lambda^\circ_{HSO_4^-} = \eta \Lambda_\pm T_{HSO_4^-}$

where: $\lambda^\circ_{HSO_4^-}$ = limiting ionic conductance in water for HSO_4^-

$\lambda^\circ_{HSO_4^-}$ = 50 at 25°C. [15]

η_0 = viscosity of pure water = 0.0094 poise @ 25°

$T_{HSO_4^-}$ = migration transference number of HSO_4^-

$\Lambda_\pm$ = equivalent conductance of solution based on the mean ionic concentration.

$$\Lambda_\pm = \frac{1000\ \kappa}{c_\pm}$$

κ = specific conductivity of the solution

$c_\pm$ = mean ionic concentration

Concentrations of the ionic species present were determined from the Raman spectra studies of Young and others [19, 20]. The results of the application of this principle are shown in Table 2. It is apparent that in most cases the approximation from the experimental measurements is about half that predicted from the limiting ionic conductance. However, the fact that the values are of the same approximate magnitude indicates that the measured values are probably a reasonable representation of the migration

of bisulfate ions in these solutions.

Table 2

Comparison of $\eta\kappa$ products

$N_{H_2SO_4}$	$c_{\pm}$	$1000\,\kappa$ [14]	η [12]	$T_{HSO_4^-}$	$\Lambda_T\,\eta$
0.31	11.5	235	.096	.14	.27
0.31	11.5	235	.096	.14	.27
0.48	12.3	123	.195	.14	.27
0.48	12.3	123	.195	.13	.25
0.48	12.3	123	.195	.11	.21
0.48	12.3	123	.195	.10	.20
0.57	10.3	128	.190	.12	.28
0.61	9.6	131	.183	.09	.30
0.82	4.1	110	.186	.12	.60
0.84	3.8	104	.191	.07	.37

$$\eta_0 \lambda^\circ_{HSO_4^-} = 0.47$$

$c_{\pm}$ calculated from data of Young, Maranville and Smith [18] on the assumption of HSO_4^- and H_3O^+ only

4. Conclusions.

The measurements made in this study, by the low value of migration transference number, tend to confirm the existence of a chain conductance mechanism in the middle concentration range for sulfuric acid solutions. If the hydronium ion is assumed to have approximately twice the mobility by migration, the chain mechanism of conductance must account for approximately two-thirds of the current carried through the solution. It is impossible to distinguish by this method of measurement which chain mechanism may in fact be carrying the current.

Since chain conductance reduces the individual ionic lifetimes, it reduces the ability of the ions to conduct by physical migration. The mechanisms of chain conductance and physical migration may thus be considered competing mechanisms for ion which may conduct by either a proton transfer chain or by migration. A model was developed utilizing the idea of competing mechanisms to predict the conductivity of sulfuric acid solutions; this model, which is empirical in nature, is presented in Appendix II. In its present state of development, the model is not satisfactory, but its qualitative agreement with published conductivities is sufficient to permit hope that it may provide a basis for development of a better model for conductance in these solutions.

BIBLIOGRAPHY

1. J. D. Bernal and R. H. Fowler, "A Theory of Water and Ionic Solution with Particular Reference to Hydrogen and Hydroxyl Ions", J. Chem. Phys., 1, 515 (1933).

2. M. Eigen and L. de Maeyer, "Hydrogen Bond Structure, Proton Hydration and Proton Transfer in Aqueous Solution", The Structure of Electrolytic Solutions (W. J. Hamer, Ed.), pp. 65-88, John Wiley and Sons, Inc., New York (1959).

3. R. J. Gillespie and S. Wasif, "Solutions in Sulfuric Acid. Part IX. The Electrical Conductivity of the Water-Sulphur Trioxide System in the Region of the Composition of Sulphuric Acid," J. Chem. Soc., 1953, 209-215, (1953).

5. R. J. Gillespie and S. Wasif, "Solutions in Sulphuric Acid. Part XI. Densities and Viscosities of Some Sulphuric Acid Solutions", J. Chem. Soc., 215-221 (1953).

6. R. J. Gillespie and S. Wasif, "Solutions in Sulphuric Acid. Part XII. Electrical Conductivity Measurements", J. Chem. Soc., 1953, 221-231 (1953).

7. S. Glasstone, K. J. Laidler, and H. Eyring, The Theory of Rate Processes, Chapter X, pp. 552-575, McGraw-Hill Book Company, New York (1941).

8. W. J. Hamer, "Temperature Variation in Transference Numbers of Concentrated Sulfuric Acid as Determined by the Galvanic Cell Method", J. Am. Chem. Soc., 57, 662-667 (1935).

9. L. P. Hammett and F. A. Lowenheim, "Electrolytic Conductance by Proton Jumps; The transference Number of Barium Bisulfate in the Solvent Sulfuric Acid", J. Am. Chem. Soc., 56, 2620-2625 (1934).

10. H. S. Harned and B. B. Owen, The Physical Chemistry of Electrolytic Solutions, 3rd Ed., Reinhold Publishing Corporation, New York (1958).

11. J. E. Kunzler and W. F. Giauque, "The Change in Electrical Conductivity of Aqueous Sulfuric Acid Near Absolute H_2SO_4 and $H_2SO_4 \cdot H_2O$", J. Am. Chem. Soc., 74, 804-6 (1952).

12. Landolt-Bornstein, Zahlenwerte und Funktionen aus Physik, Chemie, Astronomie, Geophysik, Technik, Vol. IV, Part 1, Springer-Verlag, Berlin (1955).

13. W. M. Latimer and J. H. Hildebrand, Reference Book of Inorganic Chemistry (revised Ed.), The Macmillan Company, New York (1940).

14. J. W. Mellor, A Comprehensive Treatise on Inorganic and Theoretical Chemistry (revised Ed.), The Macmillan Company, New York (1940).

15. B. B. Owen and R. W. Gurry, "The Electrolytic Conductivity of Zinc Sulfate and Copper Sulfate in water at 25°", J. Am. Chem. Soc., 60, 3074 (1938).

16. F. P. Treadwell and W. T. Hall, Analytical Chemistry, Ninth English Ed., Vol. II, pp. 522-3, John Wiley and Sons, Inc., New York (1945).

17. S. Wasif, "Properties of Sulfuric Acid Solutions. Part I. Transport Number Measurements in Sulfuric Acid and Oleum Solutions", J. Chem. Soc., 1955, 372, (1955).

18. A. Weissberger (editor), Techniques of Organic Chemistry, Vol I., Physical Methods of Organic Chemistry, Part IV, Chapter 46, pp. 3049-3111, Interscience Publishers, Inc. New York (1960).

19. T. F. Young, L. F. Maranville, and H. M. Smith, "Raman Spectral Investigations of Ionic Equilibria in Solutions of Strong Electrolytes", The Structure of Electrolytic Solutions, (W. J. Hamer, Ed.), pp. 48-63, John Wiley and Sons, Inc., New York (1959).

20. T. F. Young and G. E. Walrafen, "Raman Spectra of Concentrated Aqueous Solutions of Sulphuric Acid", Trans. Faraday Soc., 57, 34-39 (1961).

APPENDIX I

COMPOSITION OF SULFURIC ACID SOLUTIONS

To estimate the concentrations of various ionic species present in sulfuric acid solutions, the values of Young, Maranville and Smith [18] were plotted in the dilute concentration range. The values for the high concentration range were scaled from the graphical presentation of Young and Walrafen [19] and were plotted and smoothed with the values for the dilute solutions. Density data for stoichiometric concentrations were taken from Landolt-Bornstein [12]. Values from this plot were then tabulated for intervals of 0.05 mole fraction H_2SO_4 in this appendix as Table I-1.

In the development of a model for the conductance mechanism in sulfuric acid solutions a "relative abundance" was used (Appendix II); this is defined by:

$$(I\text{-}1) \qquad Y_i = \frac{c_i}{\sum_k c_k}$$

where: Y_i = the relative abundance of species i

c_i = the molar concentration of species i and subscripts i and k indicate any of the molecular or ionic species present in the solution. These relative abundances are tabulated in Table I-2.

Table I-1
MOLAR IONIC CONCENTRATIONS

Stoich. Mole % H_2SO_4	Stoich. H_2SO_4	Stoich. H_2O	Concentrations (moles/liter @ 25°C) HSO_4^-	SO_4^{--}	$H_5SO_5^+$	H_3O^+	Molecular H_2SO_4	Molecular H_2O
0	0.000	55.3	--	--	--	--	0	55.3
5	2.618	49.79	1.7	0.9	--	3.5	0	46.3
10	4.915	44.24	3.4	1.5	--	6.4	0	37.9
15	6.901	39.11	5.1	1.8	--	8.7	0	30.4
20	8.632	34.54	6.9	1.7	--	10.3	0	24.2
25	10.14	30.44	8.7	1.4	--	11.5	0	18.9
30	11.46	26.74	10.5	0.95	--	12.4	0	14.3
35	12.61	23.44	11.9	0.7	--	13.3	0	10.1
40	13.51	20.44	13.1	0.4	--	13.9	0	6.5
45	14.48	17.59	13.0	0.2	--	13.4	1.3	4.2
50	15.24	15.24	11.7	--	--	11.7	3.5	3.5
55	15.86	12.98	10.4	--	0.1	10.3	5.4	2.6
60	16.38	10.93	9.1	--	0.2	8.9	7.1	1.8
65	16.83	9.064	7.8	--	0.4	7.4	8.6	1.3
70	17.22	7.389	6.6	--	0.6	6.0	10.0	0.8

MOLAR IONIC CONCENTRATIONS

Stoich. Mole % H_2SO_4	Stoich. H_2SO_4	Stoich. H_2O	Concentration (Mole/liter @25°C.) HSO_4^-	SO_4^{--}	$H_5SO_5^+$	H_3O^+	Molecular H_2SO_4	Molecular H_2O
75	17.55	5.861	5.4	--	0.8	4.6	11.4	0.5
80	17.86	4.4.0	4.3	--	1.0	3.3	12.6	0.1
85	18.08	3.212	3.1	--	1.3	1.8	13.7	0.1
90	18.30	2.032	2.0	--	1.3	0.7	15.0	--
95	18.48	0.973	1.0	--	0.8	0.2	16.7	--
100	18.61	0.000	---	--	--	--	18.6	--

$C_{HSO_4^-}$, $C_{SO_4^{--}}$, and $C_{H_5SO_5^+}$ from published data 18, 19

$$C_{H_3O^+} = C_{HSO_4^-} + 2C_{SO_4^{--}} - C_{H_5SO_5^+}$$

$$C_{\text{molec } H_2O} = C_{\text{stoich. } H_2O} - C_{H_3O^+} - C_{H_5SO_5^+}$$

$$C_{\text{molec } H_2SO_4} = C_{\text{stoich } H_2SO_4} - C_{HSO_4^-} - C_{SO_4^{--}} - C_{H_5SO_5^+}$$

TABLE I-2
RELATIVE ABUNDANCES

Mole % H_2SO_4	Relative Abundance (%)					
	H_2SO_4	H_2O	H_3O^+	HSO_4^-	SO_4^{--}	$H_5SO_5^+$
0	--	100.0	--	--	--	--
5	--	88.4	6.7	3.2	1.7	--
10	--	77.0	13.0	6.9	3[redacted]	--
15	--	66.1	18.9	11.1	3.9	--
20	--	56.1	23.9	16.0	4.0	--
25	--	46.6	28.3	21.4	3.5	--
30	--	37.5	32.5	27.5	2.5	--
35	--	28.1	36.9	33.1	1.9	--
40	--	19.2	41.0	38.6	1.2	--
45	4.0	13.1	41.7	40.6	0.6	--
50	11.5	11.5	38.5	38.5	--	--
55	18.8	9.0	35.8	36.1	--	0.3
60	26.2	6.7	32.8	33.6	--	0.7
65	33.7	5.1	29.0	30.6	--	1.6
70	41.7	3.3	25.0	27.5	--	2.5

TABLE I-2 (Contd.)

Mole % H_2SO_4	Relative Abundance (%)					
	H_2SO_4	H_2O	H_3O^+	HSO_4^-	SO_4^{--}	$H_5SO_5^+$
75	50.3	2.2	20.2	23.8	--	3.5
80	59.1	0.5	15.5	20.2	--	4.7
85	68.5	0.5	9.0	15.5	--	6.5
90	79.0	--	3.7	10.5	--	6.8
95	89.4	--	1.1	5.3	--	4.2
100	100.0	--	--	--	--	--

APPENDIX II

A MODEL OF THE CONDUCTANCE MECHANISM IN SULFURIC ACID

In attempting to explain the mechanisms of conductance in the middle concentration range of aqueous solutions of sulfuric acid, a model was developed which permitted reproduction of the conductivity as a function of concentration to a fair degree. The model does not, in its present state of development, permit accurate reproduction of the conductivity; it also depends on a number of arbitrary assumptions regarding values of parameters which may be sufficiently in error to make significant changes in the details of the development. The basic idea behind this model, however, is believed to be sound, and it is therefore presented in the hope that further study may permit its development in a more accurate form.

Since chain conductance depends on an ion or molecule of the proper sort to participate in the chain mechanism being in the immediate vicinity of the ion which is transferring or receiving the proton, the ability for chain conductance to take place should depend on the relative numbers of the two species which are present in the solution. This is the key assumption in the development of this model. For comparing relative numbers of components present in the solutions, the "relative abundance" was defined; this is a type of mole fraction given by the following equation:

$$(II\text{-}1) \qquad Y_i = \frac{c_i}{\sum_k c_k}$$

where: Y_i = relative abundance of species i

c_i = molar concentration of species i.

and subscript i indicates an individual species from all molecular and ionic species, represented by the subscript k, present in the solution. For

the purposes of this model, the species considered were molecular sulfuric acid, molecular water, bisulfate ions, sulfate ions, hydronium ions, and solvated hydronium ions in sulfuric acid, ie. $H_3O.H_2SO_4^+ = H_5SO_5^+$ [20]. The values of the relative abundances used are tabulated in Appendix I.

A further quantity, the "complementary relative abundance", Y^*_j, is defined to be the sum of the relative abundances of all species which can participate in the proton transfer mechanism with ionic species "j". In this development these complementary relative abundances are given by:

$$Y^*_{H_3O^+} = Y_{H_2O}$$

$$Y^*_{HSO_4^-} = Y_{H_2SO_4}$$

$$Y^*_{H_5SO_5^+} = Y_{H_2O}$$

$$Y^*_{SO_4^{--}} = Y_{HSO_4^-} + Y_{H_2SO_4}$$

In the development of this model, the conductance is assumed to be the result of two competing mechanisms, ionic migration by bodily motion and chain conductance by proton transfer. The ability of an ion to participate in the migration is reduced by the shorter lifetime of an ion which results from its participation in a proton transfer. Eigen and deMaeyer [2] cite the lack of spectroscopic evidence for the existence of the hydronium ion as evidence for a short lifetime of the hydronium ion in dilute water solutions. The ability of an ion to participate in a proton transfer is proportional to the fraction of the ions or molecules in the solution with which it is capable of exchanging a proton; that is, this ability is proportional to Y^*_j. It then follows that the ability of an ion to participate in the migration should be proportional to $1-Y^*_j$.

Walden's rule is assumed to apply to the migration of ions during the ionic lifetime, hence the following relation is established:

$$\lambda_{j\,mig} = \lambda^{\circ}_{j} \frac{2}{7} (1 - Y^{*}_{j}) \qquad \text{(II-2)}$$

where: $\lambda_{j\,mig}$ = ionic conductance by migration only.

The value for λ° is equal to the normally reported values for λ° except in the case of the hydroxide ion and the hydronium ion where the chain conductance in aqueous solutions at infinite dilution is primarily by the chain conductance.

The conductivity due to proton transfer by a chain mechanism is assumed to be proportional to the fraction which that species represents of the total number of particles in the solution; that is, conductivity by the chain mechanism is proportional to Y_j. Further, the conductivity resulting from chain conductance is proportional to the rate of proton transfer, which is proportional to Y^{*}_{j}. Gillespie has found evidence that the chain mechanism is viscosity dependent [6]; although the nature of the viscosity dependence is not definitely known, the chain conductance was assumed to be inversely proportional to the viscosity of the solution. It may be assumed that the conductivity due to the chain mechanism is some function of the total concentration; it was found empirically that the best approximation with the other assumptions was that the conductivity by the chain mechanism is inversely proportional to the cube root of the total concentration. The conductivity resulting from the chain mechanism alone by an individual ionic species is thus given by:

(II-3) $$\kappa_{j\,chain} = \frac{k\, Y_j\, Y_j^*}{\eta \left(\sum_k c_k\right)^{1/3}}$$

where: $\kappa_{j\,chain}$ = conductivity of the ionic species by the proton transfer chain mechanism

k = proportionality constant.

For want of better information, k is assumed to be constant and independent of the ionic species involved. The total specific conductivity of the solution is then given by:

(II-4) $$\kappa = \sum_j \kappa_{j\,chain} + \sum_j c_j \lambda_{j\,migr.}$$

or

(II-5) $$\kappa = \frac{k}{\eta \left(\sum_k c_k\right)^{1/3}} \left(\sum_j Y_j Y_j^*\right) + \frac{\eta_o}{\rho} \sum_j c_j \lambda_j^\circ (1 - Y_j^*)$$

In applying this model, all values for λ° were obtained from published values or estimated. The published values for the hydronium ion obviously could not be used since they include both effects of chain conductance and migration. No information was available for the $H_5\ SO_5^+$ ion. The values used for the computations with this model were:

ion	λ°	
HSO_4^-	50	[12, 15]
$\frac{1}{2}\ SO_4^{--}$	80	[10]
H_3O^+	80	(assumed)
$H_5SO_5^+$	40	(assumed)

The values for the migration terms of the viscosity-conductivity product were calculated at intervals of 0.05 mole fraction H_2SO_4. These values were then subtracted from the known experimental values of the viscosity-conductivity product. The difference between these two values was then compared to the values for $\sum Y_j Y_j^*$. Comparison of these curves resulted in the final selection of the reciprocal cube root concentration dependence as the best approximation to the desired form for the curve. The value for k was determined by calculating, at intervals of 0.05 mole fraction sulfuric acid, the value of k required to fit that point. The values of k were then averaged and the average value of k was used to calculate an estimated curve. The results of these calculations are tabulated in Table II-1. The values of the conductivity and the viscosity-conductivity product estimated by the model are plotted together with the experimental values for comparison in Fig. II-1.

From the calculated values in the model, it is possible to estimate the transference numbers by these various mechanisms.

For migration conductance

(II-6) $$T_{j\,migr.} = \frac{\eta_0 \, c_j \, \lambda_j (1 - Y_j^*)}{\eta \, \kappa_{est}}$$

where $T_{j\,migr}$ = transference number of the j-th ionic species by migration only.

κ_{est} = conductivity estimated by the proposed model.

For chain conductance:

(II-7) $$T_{j\,chain} = \frac{k \, Y_j \, Y_j^*}{\left(\sum_k c_k\right)^{1/3} \eta \, \kappa_{est.}}$$

where: $T_{j\,chain}$ = transference number of the j-th ion by the proton transfer chain mechanism.

A plot of the estimated transference numbers is shown in Fig. II-2; these values are tabulated in Table II-2.

This model is at best highly speculative in its detailed form; however, the general concept of competing mechanisms is believed to be sound and possibly subject to further development. The most serious apparent discrepancy in the fit of the model to the observed values is in the concentration range more dilute than the monohydrate. The difference between the form of the experimental curve and the curve derived from the model probably indicates a significant variation between the model and a good description of the actual mechanism.

The reciprocal cube root dependence of chain conductance on the total concentration is difficult to justify. It would seem natural that the conductivity should be proportional to the actual number of charge carriers in a unit volume; this is contrary to the form of the concentration dependence used. The difference may lie in the assumption that the proportionality constant, k, is independent of the species in question. It may also be that over the concentration range the variation of the total number of charge carriers in a given volume is not significant. Then the proportionality to the reciprocal cube root of concentration is equivalent to direct proportionality to the mean distance between particle centers. It is thus possible to explain the proportionality to the reciprocal cube root of concentration as being equivalent to direct proportionality to the mean distance of charge motion per proton transfer.

The large number of interrelated and unknown variables makes it impossible to derive a model which could be justified on the basis of the conductivity data for sulfuric acid alone; by a trial and error adjustment of a number of variables it should be possible to achieve a good fit to the

known conductivity data without any assurance that the model represents the actual process. Further work with other hydrogen bonded solvents might permit development of a similar model to that worked out in this case. Correlation between solvents might then permit a more accurate development for a model of proton transfer conductance.

Table II-1
Estimation of Specific Conductivity by Model

Mole % H_2SO_4	$\sum_j \eta_0 c_j \lambda_j^\circ (1-Y_j^*)$	$1000\kappa\eta - \sum_j c_j \eta_0 \lambda_j^\circ (1-Y_j^*)$	$\frac{\sum_j Y_j Y_j^*}{(\sum_k c_k)^{1/3}}$	k	$1000(\eta\kappa)_{est.}$	$\kappa_{est.}$
0	---	---	---	--	--	--
5	1.74	9.5	.0160	593	7.9	.526
10	3.76	15.0	.0278	530	14.7	.612
15	5.82	15.4	.0360	427	19.8	.582
20	7.71	14.9	.0398	374	23.2	.484
25	9.54	13.3	.0406	327	25.3	.384
30	11.28	11.6	.0382	304	26.2	.291
35	13.13	9.7	.0333	291	26.1	.218
40	14.79	8.0	.0259	308	24.9	.161
45	14.70	9.5	.0232	409	23.8	.127
50	12.65	11.6	.0282	411	23.7	.120
55	10.99	13.1	.0326	402	23.7	.123
60	9.47	14.6	.0370	394	23.9	.129
65	7.85	15.8	.0405	390	23.6	.133
70	6.39	16.7	.0403	388	23.2	.133

Table II-1 (Contd.)

Mole % H_2SO_4	$\sum_j \eta_0 c_j \lambda_j^\circ (1 - Y_j^*)$	$1000\kappa\eta - \sum_j \eta_0 c_j \lambda_j^\circ (1 - Y_j^*)$	$\frac{\sum_j Y_j Y_j^*}{(\sum_k c_k) Y_3}$	K	$1000 (\eta K)_{est.}$	$K_{est.}$
75	4.93	17.3	.0441	392	22.1	.126
80	3.67	17.5	.0433	404	20.6	.114
85	2.30	16.7	.0391	427	17.5	.090
90	1.22	12.8	.0311	411	13.2	.063
95	0.50	3.5	.0177	198	7.4	.032
100	--	--	--	--	--	--

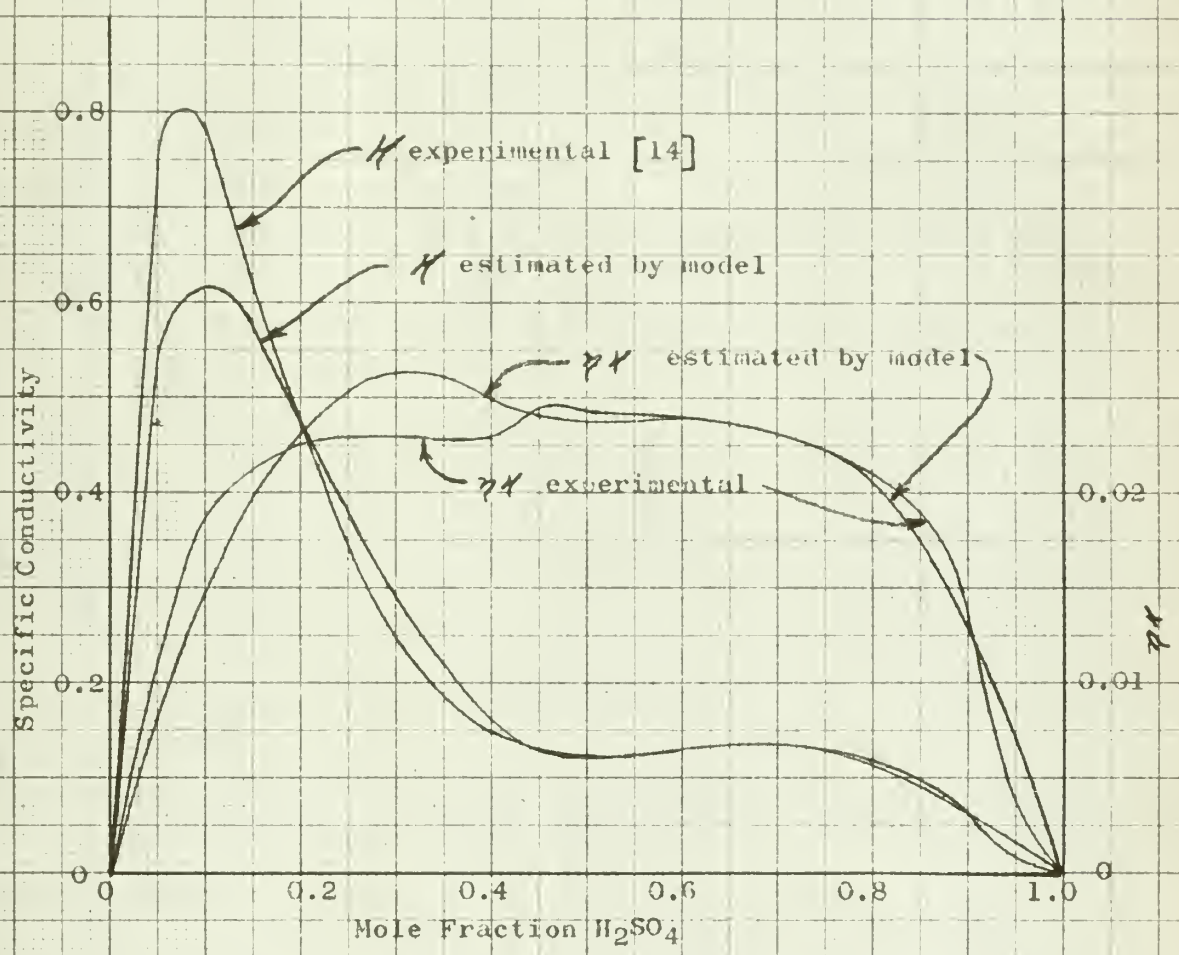

Figure II-1

Conductivity According to Model

Table II-2
Estimated Transference Numbers -- Part 1 -- Cations

Mole % H_2SO_4	Transference Numbers H_3O^+ (migr.)	H_3O^+ (chain)	$H_5SO_5^+$ (migr.)	$H_5SO_5^+$ (chain)	Total Cation
0	---	---	---	---	---
5	.035	.767	---	---	.802
10	.076	.730	---	---	.806
15	.112	.684	---	---	.796
20	.146	.639	---	---	.785
25	.183	.587	---	---	.770
30	.222	.538	---	---	.760
35	.275	.471	---	---	.746
40	.339	.382	---	---	.721
45	.369	.285	---	---	.654
50	.328	.233	---	---	.561
55	.297	.172	.001	---	.470
60	.261	.119	.003	---	.383
65	.224	.084	.006	.006	.320
70	.188	.047	.009	.006	.250

Table I-2 (Part 1) (Contd.)

Mole % H_2SO_4	Transference Numbers H_3O^+ (migr)	H_3O^+ (chain)	$H_5SO_5^+$ (migr.)	$H_5SO_5^+$ (chain)	Total cation
75	.153	.025	.014	.006	.198
80	.120	.007	.018	---	.145
85	.077	---	.028	---	.105
90	.040	---	.037	---	.077
95	.020	---	.041	---	.061
100	---	---	---	---	---

Table II-2
Estimated Transference Numbers -- Part 2 -- Anions

Mole % H_2SO_4	Transference Numbers				
	SO_4^{--} (migr)	SO_4^{--} (chain)	HSO_4^- (migr)	HSO_4^- (chain)	Total Anion
0	---	---	---	---	---
5	.084	.013	.101	---	.198
10	.071	.014	.109	---	.194
15	.061	.022	.121	---	.204
20	.046	.029	.140	---	.215
25	.032	.036	.162	---	.230
30	.020	.031	.189	---	.240
35	.013	.027	.214	---	.254
40	.008	.024	.247	---	.279
45	.003	.015	.246	.082	.346
50	---	---	.206	.233	.430
55	---	---	.166	.364	.530
60	---	---	.132	.485	.617
65	---	---	.103	.577	.680
70	---	---	.078	.672	.750

Table II-2 (Part 2) (Contd.)

Mole % H_2SO_4	Transference Numbers				
	SO_4^{--}(migr)	SO_4^{--}(chain)	HSO_4^-(migr)	HSO_4^-(chain)	Total Anion
75	---	---	.057	.745	.802
80	---	---	.040	.815	.855
85	---	---	.026	.869	.895
90	---	---	.015	.908	.923
95	---	---	.007	.932	.939
100	---	---	---	---	---

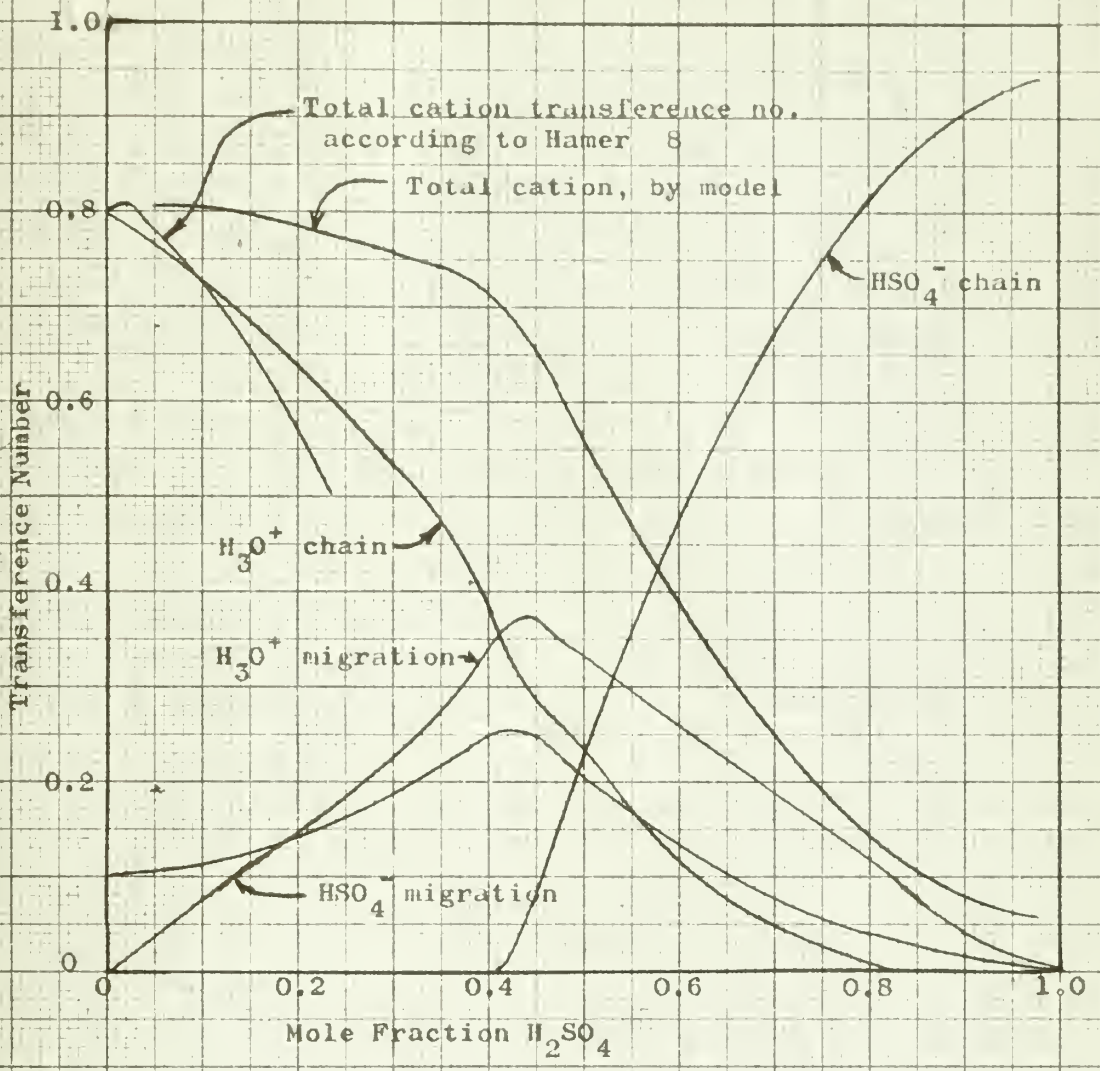

Figure II-2

Transference Numbers According to Model

thesG186
Measurement of transference numbers of t
3 2768 002 01050 6
DUDLEY KNOX LIBRARY